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LASER DYE PURITY AS DETERMINED BY THIN LAYER CHROMATOGRAPHY.(U)

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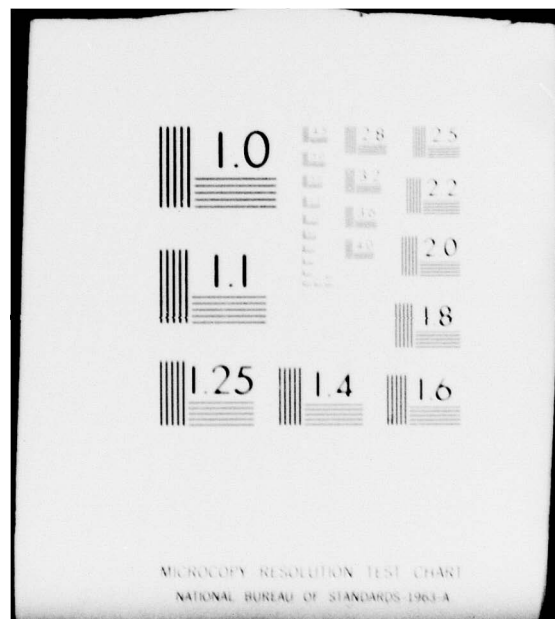
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6 **LASER DYE PURITY AS DETERMINED BY
THIN LAYER CHROMATOGRAPHY**

9 Research rept.
Nov 78 - Aug 79

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FOREWORD

The dye laser is of potential importance to the military because it offers wavelength tunability. A critical component of the dye laser is the dye solution and the way that this solution changes with useage. This report addresses the question of the purity of these laser dyes.

This study was initiated in November of 1978 and completed by August 1979. The development of the method of analysis was funded under task ZR01305. The evaluation of the purity of the dyes was funded under task ZF54-581-001 of the Electronic Material Technology Block (Program Element 62762N) at the Naval Research Laboratory.

This report was reviewed for technical accuracy by Dr. Ronald A. Henry.

Approved by
E. B. ROYCE, *Head*
Research Department
15 October 1979

Under authority of
W. B. HAFF
CAPT., U. S. Navy
Commander

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(U) *Laser Dye Purity As Determined by Thin Layer Chromatography*, by Aaron N. Fletcher and May L. Chan. China Lake, Calif., Naval Weapons Center, October 1979. 22 pp. (NWC TP 6132, publication UNCLASSIFIED.)

(U) A total of 66 laser dyes have been examined by thin layer chromatography for the presence of impurities using three different solvent systems. Very few dyes were found that could be considered as pure.

(U) The specific effect, if any, of the impurities upon the lasing characteristics of the dyes is not known. Further work is needed to determine whether a purer dye would yield better lasing characteristics. A few dyes were shown to degrade while being tested. ↩

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INTRODUCTION

The purity of chemical compounds is always a problem. This is particularly true for fluorescent compounds where high-quantum-yield impurities can yield unwanted emission. With complicated dye molecules, the problem becomes worse. Some commercial dyes have been found to be not only quite impure,¹ but in some cases were found to not even be the desired compound.^{2,3}

Impurities in laser dyes can not only absorb excitation energy but can create an even greater problem. Absorption at the lasing wavelength has a marked effect upon the output of a laser. Even one percent absorption for each cm of the dye cell can cut the output of a laser in half.⁴ In addition, transient absorption can occur when the impurity is in an electronically excited state, e.g., impurities have been reported to adversely affect long pulse output due to triplet-triplet absorption.⁵

In studies of the effects of dye purity upon lasing characteristics, increased purity has been shown to extend dye lifetime by a factor of two⁵ and the output by a factor of four.¹ Since the amounts and types of impurities are such variables, to measure the specific effects of impurities of all laser dyes would be a very large task. But where laser output and stability are important, determining the effects of impurities upon the lasing characteristics of a single dye may very well be worth the effort.

¹ P. Gacoin and P. Flamant. "High Efficiency Cresyl Violet Laser," *Opt. Commun.*, Vol. 5, No. 5 (August 1972), pp. 351-53.

² K. H. Drexhage. "What's Ahead in Laser Dyes," *Laser Focus*, Vol. 4, No. 3 (March 1973), pp. 35-39.

³ K. H. Drexhage. "Structure and Properties of Laser Dyes," in *Dye Lasers, Topics Appl. Phys.*, ed. by F. P. Schäfer. Berlin, Heidelberg, New York, Springer, 1st edition, 1973, pp. 177-78; 2nd edition, 1977, pp. 177-78.

⁴ A. N. Fletcher and D. E. Bliss. "Laser Dye Stability. Part 5. Effect of Chemical Substituents of Bicyclic Dyes Upon Photodegradation Parameters," *Appl. Phys.*, Vol. 16 (1978), pp. 289-95.

⁵ J. M. Drake and R. I. Morse. "Influence of Chemical Impurities on the Performance of a Flashlamp-Pumped Dye Laser," *Opt. Commun.*, Vol. 13, No. 2 (February 1977), pp. 109-13.

The purpose of this study was to develop an analytical method and to examine for purity a cross-section of the dyes that are sold as being "laser grade". Some of the dyes that have been prepared by Naval Weapons Center (NWC) organic chemists were also examined if their lasing characteristics had been reported previously in the open literature. A few dyes that are not sold as "laser grade" were also tested for the purpose of comparison.

EXPERIMENTAL

MATERIAL AND METHOD

A total of 66 laser dyes (mostly purchased from Eastman Kodak or Exciton Co. and a few synthesized by Dr. R. Henry or Dr. R. Atkins) were studied. They were divided into two major groups due to the major differences in chemical structure and their lasing wavelengths: Group (a): coumarins and quinolones with lasing wavelength in the range of 400-540 nm. This group contained a total of 37 dyes; Group (b): a number of commercial dyes exhibiting near infrared (IR) lasing wavelength (575-970 nm). This group contained a total of 29 dyes.

Standard thin layer chromatographic (TLC) techniques combined with three different solvent developing systems were used to successfully separate all the 66 dyes from their impurities. The routine procedure used was the following. A saturated solution of about 1 mg of each dye was prepared in 0.1 ml distilled absolute ethanol. This solution (2-3 μ l) was spotted on a 20 x 20 cm precoated silica gel G glass plate (sources are: 1. Brinkmann Instruments, Inc.; 2. Analtech Inc., and are indicated in both Tables 1 and 2). The plates were scribed with grooves and preheated one-half hour at 120°C to remove the adsorbed moisture before spotting the samples. The plates were then developed in one of the three solvent systems (about 15-40 minutes) described below.

For group (a) dyes, a solvent mixture of benzene:MeOH (90:10) was found to be very effective in separating dye and impurity. This mixture will be called Solvent System A. An ultraviolet (UV) light source was used to visualize the dye spots. A Polaroid MP-3 camera equipped with UV-17 filter (Kodak) was used to take color pictures from these developed TLC plates for record. For Group (b) dyes, two solvent systems were found to be equally useful: Solvent System B, benzene:methanol:acetic acid:H₂O (77:34:6:2), and Solvent System C, benzene:methanol (55:45). Both of these systems were used in analyses of these dyes. Since this group of dyes exhibit visible color, conventional tungsten light was used in picture taking. In order to be able to discern chromatographic spots that did not photograph well, a scribe mark was placed around each spot. Since both 250 and 365 nm UV light was used to examine all of the spots (including the Group b dyes), it was often possible to distinguish impurity spots that would otherwise be difficult to see on the photograph.

TABLE 1. Chromatographic Separation of Group (a) Dyes.^a

| Name of dye ^b | Source | Lasing wavelength (nm) | A | | A ^d | | Photobleaching and color changes |
|--|-----------------------------------|------------------------|--------------|------------------------------------|----------------|------------------------------------|--|
| | | | No. of spots | R _f values ^c | No. of spots | R _f values ^c | |
| 1 7-dimethylamino-1 methyl-4-methoxy 8-azacoumarin-2 | in-house 857-148A 3X ^f | 391 | 1 | 0.39 ^d | 1 | 0.35 ^d | ... |
| 2 7-hydroxy-4-methyl 8-azacoumarin-2 | in-house 857-13 2X ^f | 398 | 2 | 0.08 ^d 0.15 | 1 | 0.05 ^d | ... |
| 3 7-dimethylamino-1,4-dimethyl 8-azacoumarin-2 | in-house 857-45A 1X ^f | 406 | 3 | 0.38 ^d 0.3 0.25 | 2 | 0.32 ^d 0.24 | ... |
| 4 carbostyryl 124 | EK ^g 14353 | 414 | 3 | 0.15 ^d 0.23 0.26 | 1 | 0.09 ^d | ... |
| 5 Exciton L6423 | Exciton | 423 | 2 | 0.33 ^d 0.17 | 2 | 0.23 ^d 0.08 | Turned to pink (overnight) Pink to red (2 days) |
| 6 carbostyryl 165 | EK 11987 | 425 | 3 | 0.28 ^d 0.23 0.15 | 1 | 0.16 ^d | ... |
| 7 7-morpholino-4 methyl 8-azacoumarin | in-house A861-17-1 | 432 | 3 | 0.42 ^d 0.086 0.18 | 3 | 0.38 ^d 0.15 0.1 | ... |
| 8 coumarin 120 | EK | 437 | 2 | 0.38 ^d 0.25 | 2 | 0.28 ^d 0.18 | ... |
| 9 Pilot 447 (8-methyl umbelliferone) 10 ⁻³ M solution | NEC ^g | 448 | 1 | 0.27 ^d | 1 | 0.3 ^d | ... |
| 9 4-methyl-umbelliferone | EK ^h 2086 | 448 | 3 | 0.45 ^d 0.62 0.33 | 2 | 0.3 ^d 0.25 | ... |
| 10 coumarin 2 | EK 11988 | 449 | 2 | 0.53 ^d 0.38 | 1 | 0.5 ^d | ... |
| 11 coumarin 175 ^f | EK 14940 | 454 | 2 | 0.1 ^d | ... | ... | ... |
| 12 coumarin 311 | EK 14372 | 456 | 2 | 0.55 ^d 0.44 | 1 | 0.55 ^d | ... |

TABLE 1. Chromatographic Separation of Group (a) Dyes. ^a (Cont'd)

| Name of dye ^b | Source | Lasing wavelength (nm) | A | | A'd | | Photobleaching and color changes |
|--------------------------|-----------------------|------------------------|--------------|--|--------------|---|---|
| | | | No. of spots | R _f values ^c | No. of spots | R _f values ^c | |
| 13 coumarin 138 | EK 14934 | 457 | 3 | 0.6 ^e 0.48 0.2 | 3 | 0.6 ^e 0.5 0.15 | ... |
| 14 coumarin 1 | EK 2K | 459 | 2 | 0.58 ^e 0.47 | 2 | 0.6 ^e 0.47 | ... |
| 15 QaP (LD473) | 903-127 2K | 474 | 3 | 0.44 ^e 0.3 0.79 | 1 | 0.44 ^e | Turned to brownish pink (overnight) Pink to red (2 days) |
| 16 coumarin 106 | EK 14374 | 474 | 10 (streak) | 0.62, 0.29, 0.1 0.55, 0.23, 0.01 0.44, 0.2 0.36, 0.16 | 10 | 0.65, 0.3, 0.11 0.58, 0.25, 0.01 0.47, 0.22 0.38, 0.17 | ... |
| 17 coumarin 102 | EK ^h 11928 | 474 | 10 | 0.6, 0.36, 0.1 0.52, 0.25, 0.01 0.44, 0.2 0.16 | 10 | 0.6, 0.3, 0.11 0.55, 0.26, 0.9 0.47, 0.22 0.38, 0.17 | ... |
| 17 coumarin 480 | Exciton | 480 | ... | ... | 10 | 0.6, 0.37, 0.1 0.54, 0.28, 0.01 0.46, 0.25, 0.2 | ... |
| 18 Exciton LD490 | Exciton | 485 | 8 | 0.52 ^e , 0.32, 0.12 0.43, 0.22, 0.01 0.37, 0.16 | 7 | 0.52, 0.32 0.43, 0.19 0.35, 0.13 0.15 | ... |
| 19 coumarin 10 | EK 14947 | 486 | 5 | 0.35, 0.24 0.47, 0.17 0.28 | 4 | 0.33, 0.24 0.27, 0.12 | ... |
| 20 coumarin 151 | EK 14368 | 487 | 3 | 0.6, 0.17 0.38 | 2 | 0.37 ^e 0.13 | ... |
| 21 AC2F | In-house | 489 | 1 | 0.58 ^e | 1 | 0.58 ^e | ... |
| 22 AC3P | In-house 891-4 2K | 489 | 1 | 0.61 ^e | 1 | 0.61 ^e | ... |
| 23 coumarin 314 | EK 14373 | 499 | 1 | 0.25 ^e | 1 | 0.2 ^e | ... |
| 24 coumarin 307 | EK 14370 | 500 | 2 | 0.63 ^e 0.38 | 2 | 0.62 ^e 0.38 | ... |

TABLE 1. Chromatographic Separation of Group (a) Dyes.^a (Cont'd)

| Name of dye ^b | Source | Lasing wavelength (nm) | A | | A ^d | |
|--------------------------|--------------------------------|------------------------|--------------|------------------------------------|----------------|------------------------------------|
| | | | No. of spots | R _f values ^e | No. of spots | R _f values ^e |
| 25 coumarin 30 | EK 11986 | 501 | 1 | 0.27 ^e | 2 | 0.25 ^e 0.18 |
| 26 coumarin 334 | EK 14929 | 520 | 1 | 0.4 ^e | 1 | 0.4 ^e |
| 27 coumarin 337 | EK 14930 | 520 | 1 | 0.38 ^e | 1 | 0.38 ^e |
| 28 coumarin 340 | EK 14933 | 521 | 1 | 0.5 ^e | 1 | 0.5 ^e |
| 29 coumarin 7 | EK 14083 | 521 | 1 | 0.39 ^e | 1 | 0.38 ^e |
| 30 C87 | in-house RX dated 3/5/76 | 523 | 1 | 0.65 ^e | 1 | 0.65 ^e |
| 31 coumarin 152 (C2F) | EK 14369 | 524 | 2 | 0.65 ^e 0.5 | 1 | 0.65 ^e |
| 32 coumarin 6 | EK 11929 | 533 | 1 | 0.65 ^e | 1 | 0.66 ^e |
| 33 Exciton 540A | Exciton | 538 | 1 | 0.67 ^e | 1 | 0.69 ^e |
| 34 Pilot 495 | NEN | 538 | 1 | 0.64 ^e | 1 | 0.7 ^e |
| 17B coumarin 481 | Exciton | 481 | 1 | 0.79 ^e | 1 | 0.79 ^e |

Photobleaching and color changes

^a 20 x 20 cm precoated silica gel C glass plates. 0.5 mm thick (Analtech Inc.) was used.^b All dye numbers correspond to the number reported in reference 4.^c Developing time 40 minutes.^d A' is a repeat exp. of A.^e Major dye spot.^f Number of recrystallizations.^g EK represents Eastman Kodak; NEN represents New England Nuclear.^h Dye shown in Figure 2.ⁱ Coumarin 175 is a salt. Forty percent MeOH in benzene was used to separate this dye with its impurities.

TABLE 2. Chromatographic Separation of Group (b) Dyes.^a

| Name of dye | Source | Lasing wavelength (nm) | Solvent B | | Solvent C | | Photobleaching and color changes | Solution stability ^b | |
|-------------------------------------|---------------------------------------|------------------------|--------------|---|--------------|---|----------------------------------|--|-----------|
| | | | No. of spots | R _f values | No. of spots | R _f values | | Solvent B | Solvent C |
| 1 rhodamine 19 | EK 14948 ^o | 575 | 4 | 0.51, ^d 0.63 0.46 0.56 | 6 | 0.4, ^d 0.58 0.27,0.68 0.49 0.55 | None | No change | ... |
| 2 rhodamine 6G | K&K Lab | 600 | 10 | 0.52, ^d 0.45 0.84,0.21 0.48,0.91 0.36,0.59 0.40,0.79 | 10 | 0.55, ^d 0.27 0.65,0.04 0.38,0.79 0.11,0.45 0.18,0.49 | None | No change | ... |
| 3 rhodamine 6G perchlorate | Allied Chemical | 600 | 11 | 0.52, ^d 0.45 0.6,0.21,0.46 0.79,0.36,0.48 0.91,0.4,0.59 | 10 | 0.55, ^d 0.45 0.01,0.49 0.01,0.63,0.18 0.65,0.38,0.78 | None | No change | ... |
| 4 rhodamine 6G perchlorate | EK 11934 ^o | 600 | 2 | 0.51, ^d 0.48 | 2 | 0.58 ^d 0.38 | None | No change | ... |
| 5 rhodamine 6G | EK 14942 ^o | 600 | 5 | 0.51, ^d 0.57 0.47,0.59 0.44 | 5 | 0.58, ^d 0.65 0.28,0.38 0.51 | None | No change | ... |
| 6 rhodamine 3B perchlorate | EK 14945 ^o | 620 | 1 | 0.54 ^d | 2 | 0.58 ^d 0.47 | None | No change | ... |
| 7 Kiton Red S | Exciton Kiton Red 620 ^o | 589- 642 | 6 | 0.27, ^d 0.45 0.15,0.51 0.01,0.59 0.34 | 2 | 0.33 ^d 0.01 | None | No change | ... |
| 8 tetramethyl rhodamine perchlorate | EK 14946 ^o | 623 | 1 | 0.42 ^d | 1 | 0.22 ^d | None | No change | ... |
| 9 pyromin B perchlorate | EK 14950 ^o | 615- 632 | 1 | 0.45 ^d | 2 | 0.49 ^d 0.25 | None | 3 additional spots, 0.56 0.58,0.75 | ... |
| 10 rhodamine B | EK 14352 ^o | 608 | 2 | 0.5 ^d 0.45 | 3 | 0.44 ^d 0.5 | None | 5 additional spots, 0.64, 0.35,0.75, 0.44,0.59 | ... |

TABLE 2. Chromatographic Separation of Group (b) Dyes.^d (Cont'd)

| Name of dye | Source | Lasing wavelength (nm) | Solvent B | | Solvent C | | Photobleaching and color changes | Solution stability ^f | |
|---|-------------------------------------|------------------------|--------------|---|--------------|--|--|---------------------------------|----------------------------------|
| | | | No. of spots | R _f values | No. of spots | R _f values | | Solvent B | Solvent C |
| 11 3,3'-diethyl thia carbocyanine iodide | EK Lab | 625 | 1 | 0.5 ^d | 2 | 0.5 ^d 0.28 | Change from royal blue to light beige | No change | ... |
| 12 rhodamine 640 (rhodamine 101) | Exciton (basic EtOH) | 630 | 6 | 0.5 ^d , 0.54 0.12, 0.75 0.23, 0.45 | 4 | 0.38 ^d , 0.57 0.49 0.52 | None | No change | ... |
| | | 640 (acidic EtOH) | | | | | | | |
| 13 sulforhodamine 101 | EK 14318 ^o | 648 | 3 | 0.25 ^d 0.1, 0.3 | 3 | 0.26 ^d 0.01, 0.33 | None | No change | ... |
| 14 3,3'-diethylthia dicarbocyanine iodide | EK 14351 ^o | 660 | 2 | 0.47, 0.33 | 2 | 0.5, 0.24 | Change from red to brownish orange to light beige | No change | ... |
| 15 crystal violet 670 | EK 11884 ^o | 666- 709 | 4 | 0.39, 0.18 0.31, 0.75 | 4 | 0.43, 0.7 0.58, 0.19 | None | No change | ... |
| 16 Nile Blue A | EK 11953 ^o | 690 | 1 | 0.52 ^d | 2 | 0.75 ^d 0.36 | None | No change | ... |
| 17 oxazine 4 perchlorate | EK 14936 ^o | 694 | 1 | 0.42 ^d | 2 | 0.7, 0.58 (streak) | None | No change | No change |
| 18 oxazine 170 perchlorate | EK 16375 ^o | 710 | 4 | 0.48, 0.72 0.5, 0.54 | 4 | 0.78, 0.3 0.82, 0.9 (streak) | None | No change | No change |
| 19 carbazine 720 | Exciton ^o | 690- 730 | 4 | 0.72, 0.65 0.75, 0.68 | 1 | 0.9 ^d | Change from brown to brownish orange in B no color change in C | No change | No change |
| 20 oxazine 1 perchlorate | EK 11885 ^o | 715 | 1 | 0.46 ^d | 3 | 0.65, 0.5 0.3, 0.35 (streak) | None | One additional spot 0.82 | 2 additional spots, 0.95 0.75 |
| 21 oxazine-1 perchlorate (pilot 760) | New England Nuclear ^o | 690- 780 | 1 | 0.46 ^d | 3 | 0.65, 0.5 0.35 (streak) | None | One additional spot 0.82 | 2 additional spots, 0.95 0.75 |
| 22 3,3'-diethyl thia dicarbocya- nide | EK 14307 ^o | 780 | 3 | 0.52, 0.48 0.43 | 2 | 0.75 ^d , 0.82 | Color changes from blue to pinkish beige | No change | one additional spot, 0.8 |

TABLE 2. Chromatographic Separation of Group (b) Dyes.^d (Cont'd)

| Name of dye | Source | Lasing wavelength (nm) | Solvent B | | Solvent C | | Photobleaching and color changes | Solution stability ^b | |
|---|-----------------------|------------------------|--------------|--|--------------|---|--|---------------------------------|---------------------------|
| | | | No. of spots | R _f values | No. of spots | R _f values | | Solvent B | Solvent C |
| 23 3,3'-diethyl oxatricarbonyl cyanine iodide | EK 14354 ^c | 780 | 3 | 0.53, ^d 0.5 0.42 | 4 | 0.75, ^d 0.9 0.79 | Color changes from blue to grey to tan | One additional spot, 0.69 | one additional spot, 0.81 |
| 24 1,1'-diethyl-2,2'-dicarbocyanine iodide | EK 9618 | 760-790 | 1 | 0.52 ^d | 1 | 0.82 ^d | Color changes from blue to pinkish beige | No change | one additional spot, 0.81 |
| 25 3,3'-diethyl thia tricarbo-cyanine iodide | EK 14306 ^c | 860 | 7 | 0.52, ^d 0.49 0.27,0.7 0.34,0.39 0.44 | 6 | 0.8, ^d 0.6 0.75,0.82 0.9,0.7 | Color change from blue to grey to tan | No change | No change |
| 26 IR-125 ^e | EK 14400 ^c | 940 | 2 | 0.35, ^d 0.44 | 1 | 0.58 ^d | Change from bright green to greyish blue | one additional spot, 0.55 | No change |
| 27 IR-144 ^e | EK 14403 ^c | 946 | 2 | 0.46, ^d 0.62 | 1 | 0.55 ^d | Change from blue to purplish brown | one additional spot, 0.55 | No change |
| 28 IR-140 ^e | EK 14402 ^c | 950 | 3 | 0.45, ^d 0.6 0.72 | 3 | 0.85, ^d 0.91 0.82 | Change from blue to purplish brown | two additional spots, 0.8,0.55 | No change |
| 29 IR-137 ^e | EK 14401 ^c | 972 | 4 | 0.64, ^d 0.76 0.72,0.71 | 2 | 0.4, ^d 0.9 | Change from blue to grey | No change | No change |

^a Silica gel C precoated glass plates from Brinkman Instruments, Inc. was used; developing time 15-20 minutes.

^b After one week stored in a refrigerator in an ethanol or DMSO solution.

^c Laser grade material.

^d Major dye spot.

^e Dye No. 26, 27, 28, and 29 were found to be quite insoluble in EtOH. DMSO was used in place of EtOH to dissolve these dyes.

RESULTS

1. Group (a) Dyes

All 35 dyes were very well separated from their impurities using Solvent System A with the exception of coumarin 175 as shown in Figures 1 and 2. Coumarin 175 dye is a salt and the more polar Solvent System C was used to analyze this dye. Among Group (a) dyes, 14 were found to be pure (40%) and the others were found to have from 1 to 9 impurities present in the samples (see Table 1). Coumarin 106 (Eastman Kodak), coumarin 102 (Eastman Kodak), and coumarin 480 (Exciton), for example, were found to have a large number of impurities.

The amount of material applied to the TLC plate can make a significant difference in the number of impurities that are "observed". Thus, a different number of impurity spots can be observed between A and A' of Table 1 even though A' was to be a duplicate of A.

It is very interesting to observe that Exciton 423 and Q6F (LD 473) dye spots turned from colorless to pink then to red in one to two days when the plates were left exposed in air at room temperature. Further, TLC studies on the color Q6F sample indicated that at least 4 photodegradation products were formed, one of them having a very bright cherry red color.

2. Group (b) Dyes

The TLC results of Group (b) dyes are listed in Table 2 and are shown in Figures 3-10. Only 4% of Group (b) dyes could be classified as pure. Although all 29 dyes were separated from their impurities in both solvent systems, Solvent System B gave somewhat better separation for the longer wavelength dyes, while Solvent System C gave better separation for the shorter wavelength rhodamine dyes. Among the 29 dyes studied, only 2 dyes were found to be pure. Carbazine 720 (Dye 19, Figure 4) appeared to be pure in Solvent System C; however, the same dye revealed four components in Solvent System B and the color also changed from dark brown to orange. It is possible that the dye had reacted with the solvent, e.g., acetic acid, to produce the observed additional spots. Other non-acidic solvent systems should be designed to further investigate the purity of this dye.

Various substituted carbocyanine dyes with a general chemical structure of $R(-CH=CH-CH_2)_j-R$ exhibited photobleaching phenomena. The blue-green colors faded shortly after the plate was spotted and developing initiated. The rate of color fading depended on the amount of dye that was present in the spot. It is well known that these polymers are very unstable chemicals, and such dyes could very easily react with oxygen in the presence of light. Any reactions at the double bonds reduce the degree of conjugation and thus bleaching occurs.

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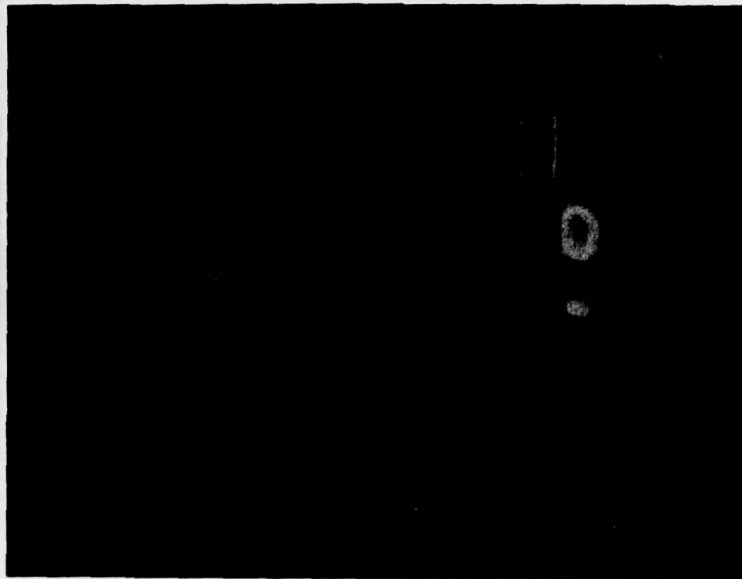


FIGURE 1. Group (a) Dyes 1-17B Developed by Solvent A.

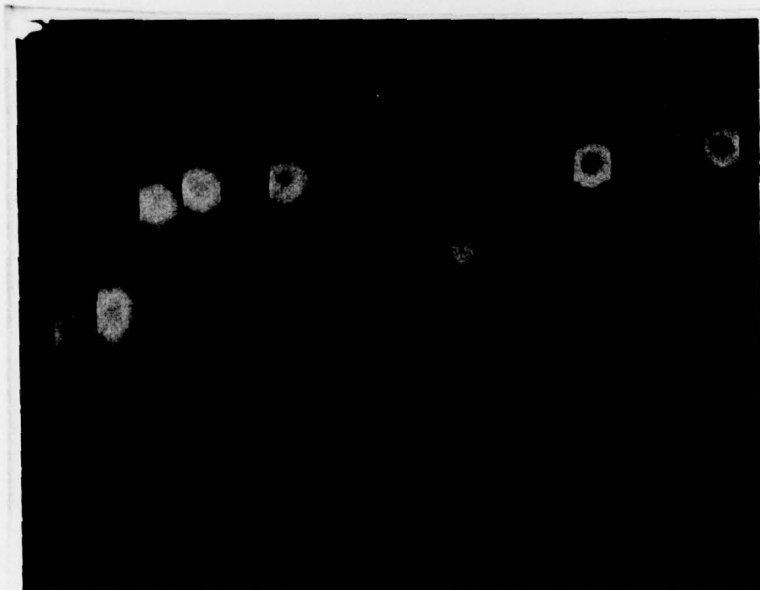


FIGURE 2. Group (a) Dyes 18-34 Developed by Solvent A.

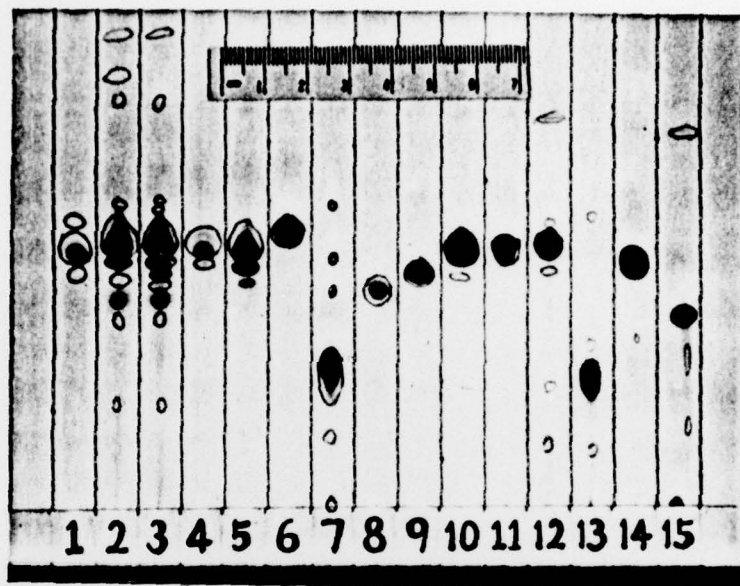


FIGURE 3. Group (b) Dyes 1-15 Developed by Solvent B.

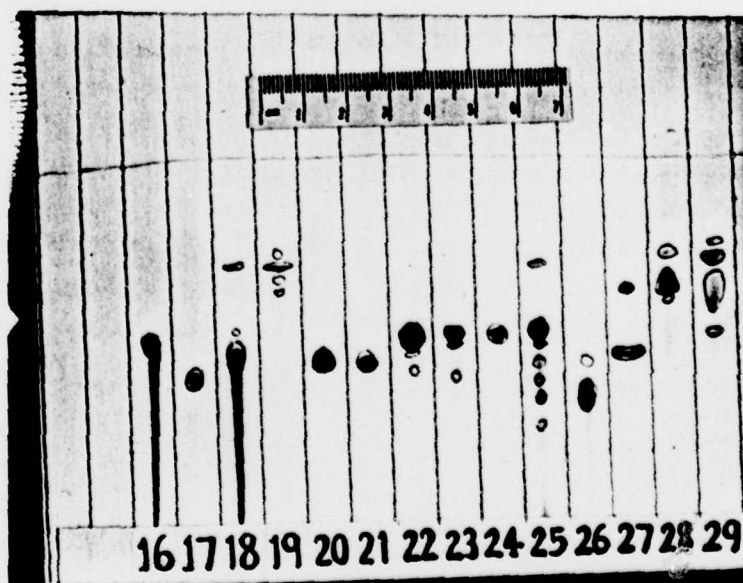


FIGURE 4. Group (b) Dyes 16-29 Developed by Solvent B.

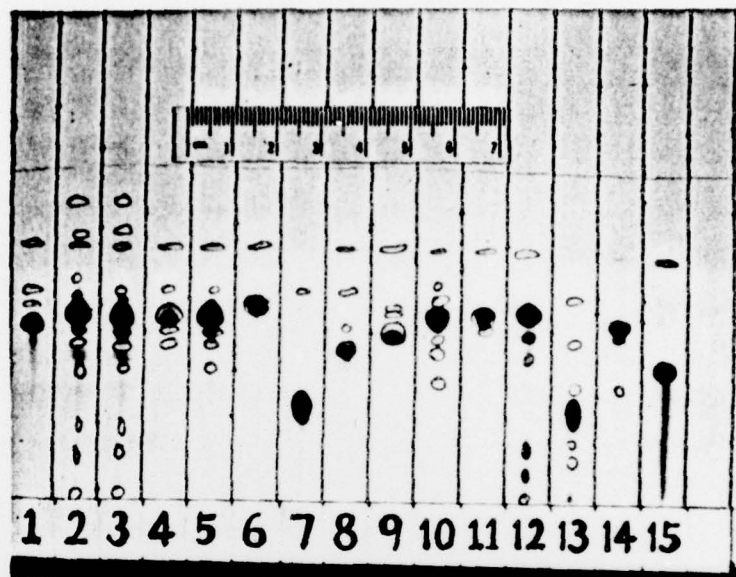


FIGURE 5. Group (b) Dyes 1-15, One Week Old Solution, Developed by Solvent B.

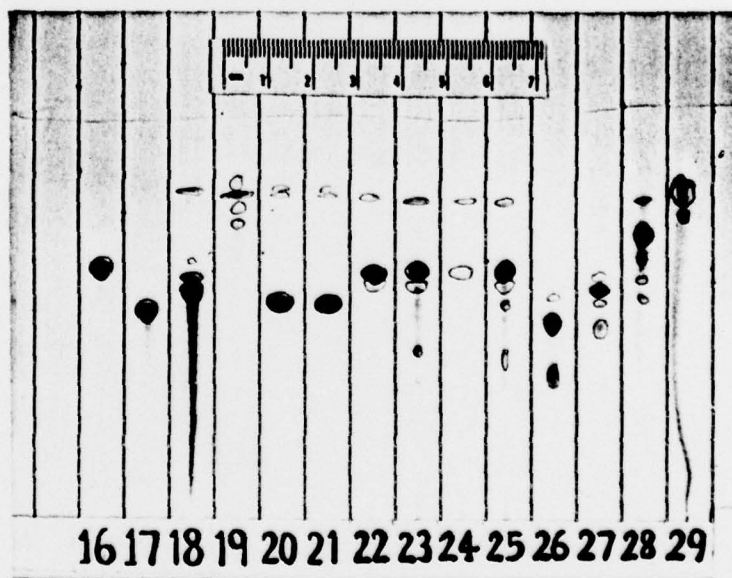


FIGURE 6. Group (b) Dyes 16-24, One Week Old Solution, Developed by Solvent B.

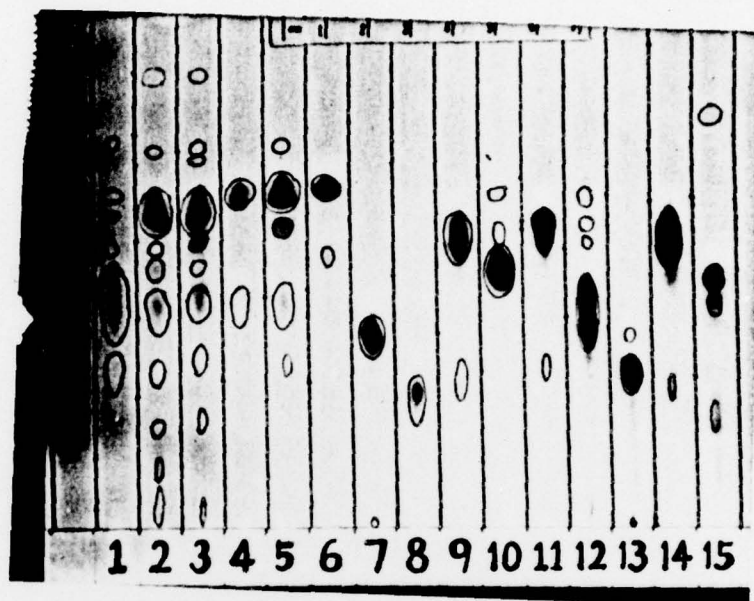


FIGURE 7. Group (b) Dyes 1-15 Developed by Solvent C.

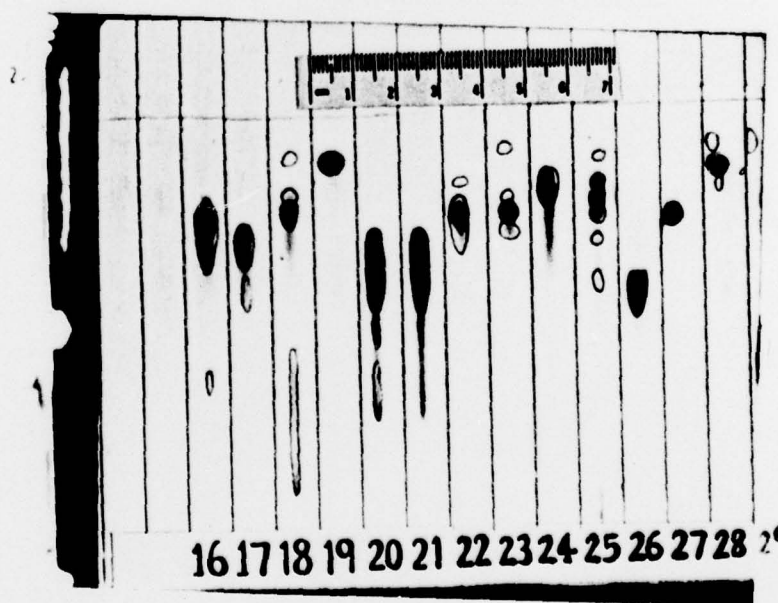


FIGURE 8. Group (b) Dyes 16-29 Developed by Solvent C.

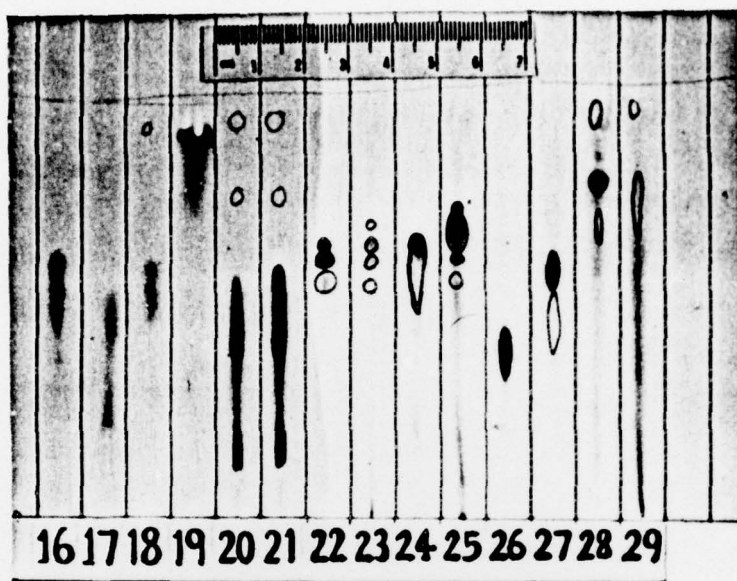


FIGURE 9. Group (b) Dyes 16-29, One Week Old Solutions, 10 Minutes After Being Developed by Solvent C.

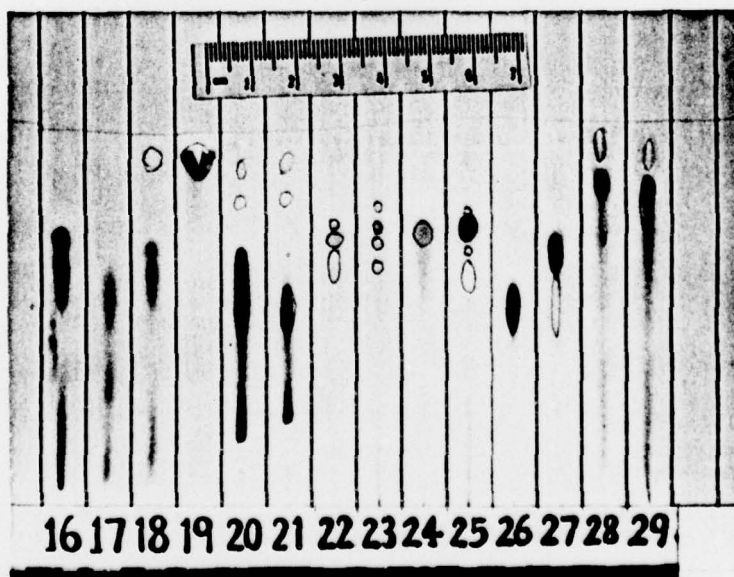


FIGURE 10. Group (b) Dyes 16-29, One Week Old Solution, Four Hours After Being Developed by Solvent C.

DISCUSSION

The Group (a) dyes were found, on the whole, to be much purer than those of Group (b), and yet only 40% of Group (a) dyes were found to show no impurities. Two points must be emphasized, however. The first is that the TLC technique is qualitative in nature; some or all of the impurities may be in trace amounts. The second and most important point is that the effect of these impurities upon the lasing characteristics of the dye solutions have not been determined. Dyes lase quite effectively in contact with high concentrations of non-dye molecules — namely the solvent. Thus a more extensive study is needed to determine the overall effect of the impurities observed in this study.

Some effort was made to determine the effects of the test method upon the generation of what would appear to be impurities. As mentioned in the Results, the apparent impurities of carbazine 720 may be due to a reaction with acetic acid. Figures 5 and 6 show the effect of TLC on week-old solutions stored in the dark in a refrigerator as opposed to fresh solutions shown in Figures 3 and 4. There appears to be a small amount of impurity having high Rf values in most of the week-old solutions that is not apparent in the fresh solutions. Dye 11 in Figure 5 shows a second red spot not seen in Figure 3. Similarly, dyes 12, 13, 27, and 28 in Figures 5 and 6 show additional spots not observed in Figures 3 and 4. Thus, TLC could be used to follow the interaction of the dyes with their solvents and/or air fairly independent of their photochemical reactions.

Since light is used to examine the TLC plates, the techniques used here are not completely free from photochemical reactions. The photochemical effect is particularly noticeable in Figures 8-10 for dyes 22 through 28. Marked color change occurred four hours after the development of these solutions. This effect may have been accelerated through interaction with the solvent in the week-old solutions shown in Figures 9 and 10.

The effect of the silica gel substrate upon the degree of photo-degradation is always a question. But the rapid change in color of dyes exposed to room light is certainly suggestive that such dyes will probably degrade rapidly when exposed to a xenon flashlamp.

Of particular interest to the user of laser dyes is whether an expensive "laser grade" dye is better than the standard commercial material. Dyes 2-5 in Figures 5 and 7 indicate that the laser grade dyes 4 and 5 have much fewer impurities than do the regular commercial grade dyes 2 and 3. Similarly, the laser grade sample of 4-methyl umbelliferone (Dye 9, Table 1) is found to be pure in contrast to the non-laser grade Eastman Kodak material.

SUMMARY

Three TLC solvent systems were developed in analyzing large numbers of dyes with vastly different chemical structures, namely quinolones, coumarins, rhodamines, carbazines, carbocyanines, oxazines, etc. These comprised dyes exhibiting lasing wavelength ranging from 400-970 nm. The method is easy, fast and reproducible. It provided a good qualitative analytical procedure for determining dye purity and also gave information about the stability of dyes toward solvent, light, air, or combination of any of these three factors. However, the method does not offer detailed quantitative data. High pressure liquid chromatography (HPLC) would be an ideal instrument for both qualitative and quantitative results.

Whether trace impurities have very much to do with the lasing characteristics of dyes is a very interesting problem which remains to be investigated.

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